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$Li(OHCH_2CH_2NH_2)(CF_3OAC)$: A novel and homogeneous acidic ionic liquid catalyst for efficient synthesis of 2-amino-4*H*-chromene derivatives

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ABSTRACT

The ionic liquid $Li(OHCH_2CH_2NH_2)(CF_3OAC)$ was found to efficiently catalyze the three-component reaction between different enols, aldehydes, and malononitrile, leading to rapid synthesis of 2-amino-4*H*-chromene derivatives in fairly high yields. The catalyst is easily prepared, highly stable, simple to handle and recycled for several times without significant loss of activity. The method is simple, starts from readily accessible commercial starting materials, and provides biologically interesting products in good yields and short reaction times. The desired ionic liquids, for aromatic aldehyde leads to get the products. Heating was very effective in increasing the efficiency of the product and in the presence of heat, the desired products were created in a shorter time.

Keywords: *Lithium, Ionic liquid, Chromene derivatives, Reusable catalyst.*

1. Introduction

In the synthesis of multicomponent reaction, various solvents have been used, such as ethers, amines, alcohols [1] and other volatile organic compounds for applications like extraction, absorption, azeotropic distillation etc. These solvents have their own limitations such as environmental issues, recycle ability, etc. These limitations can be overcome by the use of ionic liquids. Thus, ionic liquids have been studied for their possible application in relation to green chemical processes. Ionic liquids (ILs) have large liquid range, high thermal stability, nonflammability under ambient conditions, wide electrochemical window, and strong ability to dissolve many organic or inorganic solutes [2-5]. Notably, ILs can be tailored to meet particular physical and chemical demands, and increase the selectivity and reactivity of various transformations [6-9]. The chromene moiety, including that of 2*H*-chromene and 4*H*-chromene, belongs to a major class of natural oxygen-containing heterocyclic compounds, which are widely found in edible fruits and vegetables [10]. These compounds have wide range of biological and pharmacological properties, such as diuretic, anti-cancer, anticoagulant, anti anaphylactic, antioxidant, antileishmanial, antibacterial, antifungal, hypotensive, anticoagulant, antiviral, diuretic, antiallergenic, and antitumor activities [11]. A number of methods have been reported for the synthesis of these compounds in the presence of different homogeneous or heterogeneous catalysts such TMGT [12], γ-Fe_2O_3@HAp-Si-$(CH_2)_3$-AMP [13], TBAB [14], SDS [15], DBU [16], $[H_6[P_2W_{18}O_{62}].18H_2O$ [17], DAHP [18], Hexamethylenetetramine [19], CuO nanoparticles [20], $RuBr_2(pph_3)_4$ [21]. However, many of these methods are associated with several disadvantages such as long reaction time, drastic reaction conditions, difficult catalyst recovery, very expensive reagents, low yields and tedious workup. Therefore, introduction of clean procedures and utilizing ecofriendly green and recyclable catalyst have attracted more attention.

Having the above points in mind, we report here our results on the efficient synthesis of 2-amino-4*H*-chromene with diverse substituents in the presence of a catalytic amount of $Li(OHCH_2CH_2NH_2)(CF_3OAC)$ ionic liquid under solvent-free conditions (Schemes 1).

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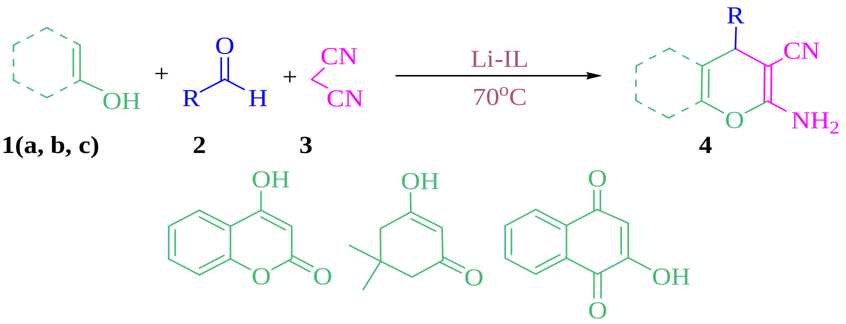


1(a, b, c) 2 3 4

1a 1b 1c

Scheme 1. One-pot three-component reaction of different enols, aldehydes, and malononitrile catalyzed by $Li(OHCH_2CH_2NH_2)(CF_3OAC)$ ionic liquid.

2. Experimental

2.1. Materials and equipment's

Chemicals were purchased from Merck and Fluka Chemical Companies and used without further purification. The purity determination of the products was accomplished by TLC on silica gel polygram SIL G/UV 254 plates. All products were confirmed by their m.p., IR, NMR and comparison with data in the pointed references. Melting points were determined on an electrothermal type 9200 melting point apparatus. IR spectra were recorded using a Shimadzu IR-470 spectrometer with KBr plates. In all the cases the ^{1}HNMR spectra were recorded with Bruker Avance 300 MHz instrument. Chemical shifts are reported in parts per million in DMSO with tetramethylsilane as an internal standard. The ^{13}CNMR data were collected on Bruker Avance 75 MHz instrument. Mass spectra were recorded on a shimadzu QP1100EX mass spectrometer operating at an ionization potential of 70eV. Inductively coupled plasma optical emission spectrometry (ICP-OES) measurements were performed on an ICP varian 735-ES.

2.2. General procedure for the preparation of $Li(OHCH_2CH_2NH_2)(CF_3OAC)$

At the first time, freshly distilled trifluoromethane-acetate (3 g, 26.5 mmol) was added to (3 g, 71 mmol) of LiCl in a 20 ml magnetically stirred glass vial during 3h at room temperature. The solid metal salt Li (CF_3OAC) was separated from the reaction mixture by decanting and washed with diethylether (2×20 ml) and dried at 100 °C to obtain refered product (2.8 g). ICP-OES analysis of the obtained $Li(CF_3OAC)$ has revealed a concentration of (0.188 g) of Li^+ being equal to (31.3 mmol) of Li^+ in the $Li(CF_3OAC)$. In the second step, a sample of recrystallized Li (CF_3OAC) (2 g, 16.6 mmol) and $NH_2CH_2CH_2OH$ (2.5 g, 40 mmol) was added together and then heated to 115 °C in an oven for 10 min. Solvent of the collected organic phase was removed by ultrasound for 15 min and the solution was again heated to 115 °C for 15 min (yield > 99%). Atomic absorption analysis of this liquid has shown that it is 0.03 mol% in concentration of dissolved Li^+ ion.

2.3. General procedure for the preparation of 2-amino-4H-chromene derivatives (4, 5, 6)

A mixture of an aromatic aldehyde (1 mmol), malononitrile (1 mmol), enolizable compound (1a, 1b, 1c, 1 mmol) and $Li(OHCH_2CH_2NH_2)(CF_3OAC)$ (1 ml) was stirred under heating conditions for appropriate time. After completion of the reaction, the mixture was cooled to room temperature. The solid product was collected by filtration, washed with water and aqueous ethanol and purified by recrystallization from ethanol. The recovered catalyst was dried and reused for subsequent runs.

2.4. General procedure for the separation of $Li(OHCH_2CH_2NH_2)(CF_3OAC)$

For this aim, after completion of the reaction (monitored by TLC), water was added to the reaction mixture and then the solid was isolated by filtration. The ionic liquid in water could be recovered easily by evaporation at 80 °C in a vacuum. The recovered IL was washed with diethyl ether and dried at 80°C in a vacuum for 1h.

Selected spectral data

*2-amino-4-(3-hydroxyphenyl)-5-oxo-4,5-dihydropyrano [3,2-c]chromene-3-carbonitrile (**4p**):*

IR (KBr): $\bar{\nu}$ = 3337, 3283, 3246, 3163, 2183, 1676, 1632, 1379 cm^{-1}. ^{1}HNMR (400 MHz, DMSO-d$_6$): δ= 4.40 (s, 1H), 6.57-6.59 (m, 2H), 6.63 (d, 1H), 7.07 (dd, 1H), 7.25 (s, 2H), 7.30 (dt, 1H), 7.34 (d, 1H), 7.58 (dt, 1H), 7.90 (dd, 1H), 9.30 (s, 1H) ppm. ^{13}CNMR (100 MHz, DMSO-d$_6$): δ= 36.99, 58.32, 110.17, 112.46, 114.21, 114.51, 115.83, 118.48, 120.34, 122.16, 122.46, 129.79, 131.67, 138.21, 146.23, 151.65, 157.82, 159.43, 160.92 ppm.

3. Results and Discussion

3.1. Catalyst characterization

3.1.1. IR analysis

We characterize the ionic liquid by infrared (IR) spectroscopy for the first time. In the IR spectrum, the OH stretching vibration is embedded in in the 3200-3600 cm^1 range. The broad band centered at 1650 cm^1 is a combined band of the carbonyl stretching and N-H plane-bending vibrations, while the N-H stretching vibrations are perceived as very weak bands at 3270 and 3450 cm^1.

3.1.2. ICP analysis

Inductively coupled plasma optical emission spectrometry (ICP-OES) indicates the leachable portion of the elements in (Table 1). This method proves that Lithium has been intercalated into trifluoroacetate interlayer spaces.

In continuation of our research on the development of environmentally friendly procedures for the synthesis of biologically active heterocyclic molecules [22,23], we decided to investigate the possibility of synthesizing various 2-amino-4*H*-chromene derivatives by one-pot three-component condensation of malononitrile with aldehydes and some cyclic 1,3-dicarbonyl compounds in ionic liquid as a catalyst-solvent. The products were obtained in high yields by a simple work-up (Scheme 1). In order to determine the optimum condition, we investigated the reaction of 4*H*-chromene (1 mmol), benzaldehyde (1 mmol) and malononitrile (1mmol) using $Li(OHCH_2CH_2NH_2)(CF_3OAC)$ at variable temperatures and alternatively in closely related ionic liquids (Table 2).

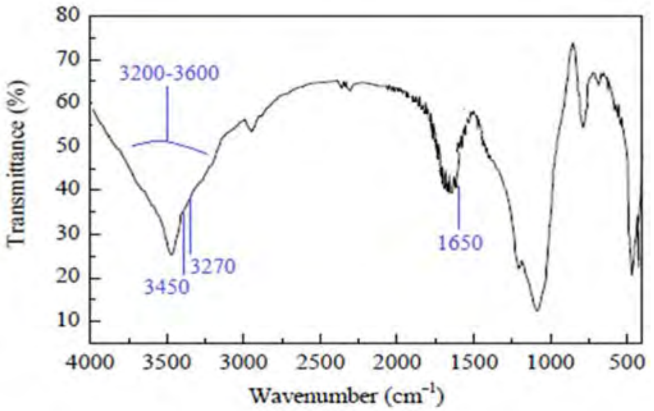


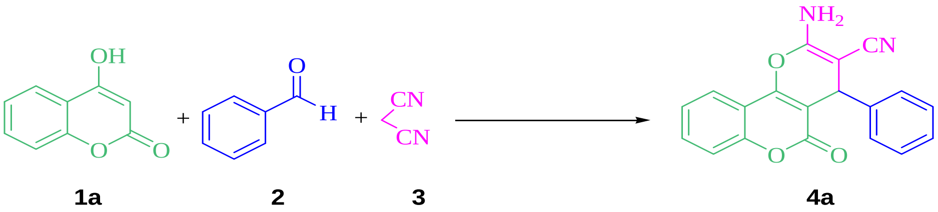
Fig. 1. IR spectra of $Li(OHCH_2CH_2NH_2)(CF_3OAC)$.

Table 1. ICP analysis with ME-01 Elements Method.

Element	DL[a]	Leachable Portion
Li	1	34016

[a]DL: Detection Limit (in ppm).

Table 2. Influence of different catalysts on the reaction of 4-hydroxycoumarin, benzaldehdye and malononitrile.



Entry	Catalyst	Reaction time	Yield(%)[a]
1	---	200 min	trace
2	$TMGT_f$	4 h	17
3	[BMPy]Cl	15 min	26
4	Et_4NBr	120 min	32
5	[BMIm] BF_4	120 min	40
6	[BMIm] BF_4 / *p*-TSA	25 min	75
7	[2-aemim][PF_6]	25 min	80
8	[BMIm] HSO_4	120 min	84
9	$Li(OHCH_2CH_2NH_2)(CF_3OAC)$ (60 °C)	7 min	70
10	$Li(OHCH_2CH_2NH_2)(CF_3OAC)$ (70 °C)	5 min	94
11	$Li(OHCH_2CH_2NH_2)(CF_3OAC)$ (80 °C)	7min	87

[a]Isolated yield.

It could be seen that the best result was obtained with 1mL of Li($OHCH_2CH_2NH_2$)(CF_3OAC) at 70 ˚C (Table 2, entry 10). Increase or decrease reaction temperature did not improve the yield of the product (Table 2, entry 9 and 11). The results show that $TMGT_f$ and basic ionic liquids such as [BMPy]Cl and Et_4NBr produce low yields of products and the reaction time is longer than acidic ionic liquids (17-32%), (Table 2, entry 2-4). The neutral ionic liquid, [BMIm]BF_4, was not as effective as Li($OHCH_2CH_2NH_2$)(CF_3OAC), however, it found comparable catalysis activity when contaminated with 20 mol% of *p*-TSA (Table 2, entry 5 and 6). Among various other catalysts, [BMIm]BF_4, [BMIm] BF_4 / *p*-TSA afforded poor to moderate yields (40-75%) (Table 2, entry 5 and 6), while, [2-aemim][PF_6] and [BMIm]HSO_4 gave good yields of the desired products (80-84%) (Table 2, entry 7 and 8). After optimization of the reaction conditions, various aromatic aldehydes were subjected to react with different enols **1** and malononitrile **3** under the selected conditions. The reactions proceeded with different aldehydes substituted with electron-donating or electron-withdrawing groups giving excellent yields. From the above observations, it is evident that the Li($OHCH_2CH_2NH_2$)(CF_3OAC) has successfully accommodated wide range of aromatic aldehydes possessing broad array of functional groups and substitution patterns. The formations of products were confirmed by physical and spectroscopic data and are in good agreement with reported one. The simple experimental and product isolation procedure combined with ease of recovery and reusability of ionic liquid is expected to the development of green strategy for the synthesis of pyranochromenes. Also, Similar results in case of another 1,3-dicarbonyl compounds such as dimedone and 2-hydroxynaphthalene-1,4-dione is obtained. The desired products were obtained in good to excellent yields in short reaction times. The results were summarized in Table **3**, **4**, **5**.

Table 3. Three component synthesis of 2-amino-3,4-dihydropyrano[3,2-*c*]chromene derivatives from the reaction of 4-hydroxycoumarin, aldehydes and malononitrile in the presence of a catalytic amount of ionic liquid.

Entry	Product	Aldehyde	1,3-Diketone	Yield (%)[a]	Time (min)	m.p. (°C)		Ref.
						Found	Reported	
1	4a	C_6H_5	1a	94	5	257-259	(256-258)	[15]
2	4b	2,4-di-Cl-C_6H_3	1a	94	5	256-258	(255-257)	[13]
3	4c	4-NO_2-C_6H_4	1a	93	6	251-253	(250-252)	[13]
4	4d	3-Cl-C_6H_4	1a	92	6	242-244	(243-245)	[14]
5	4e	2-Cl-C_6H_4	1a	95	6	245-246	(244-246)	[24]
6	4f	3-Pyridyl	1a	92	7	254-256	(255-257)	[13]
7	4g	2,3-di-Cl-C_6H_3	1a	90	5	280-282	(281-283)	[13]
8	4h	4-Pyridyl	1a	90	7	271-273	(270-272)	[13]
9	4i	3–NO_2-C_6H_4	1a	91	6	259-261	(260-262)	[13]
10	4j	4–F-C_6H_4	1a	93	5	258-259	(260-262)	[15]
11	4k	2-Furyl	1a	90	7	250-251	(251-253)	[14]
12	4l	4-MeO-C_6H_4	1a	91	6	220-222	(221-223)	[24]
13	4m	3,4-di-MeO-C_6H_3	1a	90	6	227-229	(228-230)	[15]
14	4n	2–Me-C_6H_4	1a	92	7	258-260	(260-262)	[15]
15	4o	4–Me-C_6H_4	1a	92	7	253-255	(252-254)	[15]
16	4p	3–OH-C_6H_4	1a	93	6	275-277	-	-
17	4q	4–OH-C_6H_4	1a	96	5	259-260	(259-261)	[25]

[a] Isolated yields.

Table 4. Three component synthesis of 2-amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4*H*-benzo[*b*]pyran derivatives from the reaction of dimedone, aldehydes and malononitrile in the presence of a catalytic amount of ionic liquid.

Entry	Product	Aldehyde	1,3-Diketone	Yield (%)[a]	Time (min)	m.p. (°C)		Ref.
						Found	Reported	
1	5a	C_6H_5	1b	94	6	227-229	(230-231)	[26]
2	5b	4-MeO-C_6H_4	1b	90	8	220-222	(221-223)	[26]
3	5c	4–Me-C_6H_4	1b	93	7	227-229	(228-230)	[29]
4	5d	4-NO_2-C_6H_4	1b	90	5	177-179	(179-180)	[27]
5	5e	3-NO_2-C_6H_4	1b	92	7	213-215	(214-216)	[28]
6	5f	4–F-C_6H_4	1b	92	5	210-212	(210-211)	[32]
8	5h	4-Cl-C_6H_4	1b	93	4	216-218	(215-217)	[27]
9	5i	2-Cl-C_6H_4	1b	95	4	213-215	(214-215)	[29]
10	5j	4-OH-C_6H_4	1b	91	3	223-225	(224-226)	[27]
11	5k	2,4-di-Cl-C_6H_3	1b	95	5	237-239	(238-240)	[26]
12	5l	4–Br-C_6H_4	1b	90	4	270-272	(269-271)	[28]
13	5m	2-Thienyl	1b	93	9	223-225	(224-226)	[33]
14	5n	2-Furyl	1b	94	7	221-223	(220-223)	[34]
15	5o	4-N(Me)$_2$-C_6H_4	1b	91	9	209-211	(210-212)	[30]

[a]Isolated yields.

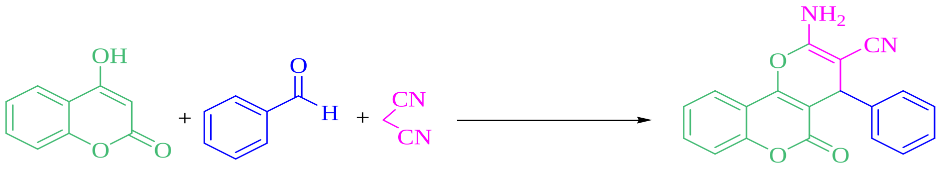
Table 5. Three component synthesis of 2-amino-3-cyano-4-aryl-5,10-dioxo-5,10-dihydro-4*H*-benzo[*g*]chromene derivatives from the reaction of 2-hydroxynaphthalene-1,4-dione, aldehydes and malononitrile in the presence of a catalytic amount of ionic liquid.

Entry	Product	Aldehyde	1,3-Diketone	Yield (%)[a]	Time (min)	m.p. (°C)		Ref.
						Found	Reported	
1	6a	C_6H_5	1c	94	12	260-262	(261-262)	[35]
2	6b	3-MeO-C_6H_4	1c	90	14	245-247	(247-248)	[37]
3	6c	4-MeO-C_6H_4	1c	93	13	246-248	(247-248)	[36]
4	6d	3,4-di-MeO-C_6H_3	1c	95	12	269-271	(270-271)	[38]
5	6e	2,3,4-tri-MeO-C_6H_2	1c	92	13	289-291	(290-293)	[38]
6	6f	4-OH-3-MeO-C_6H_3	1c	92	10	242-244	(243-245)	[36]
7	6g	4-Cl-C_6H_4	1c	92	10	249-251	(249-252)	[35]
8	6h	2-Cl-C_6H_4	1c	93	9	238-240	(236-239)	[36]
9	6i	2,4-di-Cl-C_6H_3	1c	95	9	285-287	(286-288)	[39]
10	6j	4-OH-C_6H_4	1c	91	8	256-258	(257-258)	[36]
11	6k	3–Br-C_6H_4	1c	92	12	258-260	(259-260)	[37]
12	6l	4–Br-C_6H_4	1c	90	9	252-254	(253-255)	[35]
13	6m	4–Me-C_6H_4	1c	90	10	241-243	(242-244)	[35]
14	6n	2-NO_2-C_6H_4	1c	95	7	241-243	(242-244)	[39]
15	6o	3-NO_2-C_6H_4	1c	92	9	246-248	(247-249)	[37]
16	6p	4-NO_2-C_6H_4	1c	94	6	233-235	(234-235)	[36]
17	6q	4–F-C_6H_3	1c	93	7	241-243	(240-242)	[36]

[a]Isolated yields.

To compare the efficiencies of this ionic liquid system, we have gathered the results obtained by using this ionic liquid and those reported on the application of some other catalysts to the synthesis of 3,4-dihydropyrano[*c*]chromenes **4a** in Table 3. The applied catalysts such as TMGT, γ-Fe_2O_3 @ HAp-Si-$(CH_2)_3$-AMP, TBAB, SDS, DBU, $H_6[P_2W_{18}O_{62}].18H_2O$, DAHP, Nano aluminum hydroxide, CuO nanoparticles and $RuBr_2(pph_3)_4$ were not found as effective as $Li(OHCH_2CH_2NH_2)$ (CF_3OAC). Different catalytic activities depend on catalyst structures, acid/base strength and also the electronic properties. The activity of $Li(OHCH_2CH_2NH_2)(CF_3OAC)$ is better conceived by considering its acid/base bifunctional nature, providing both donating and accepting functions during the catalysis process. However, many proposed methods for the synthesis of these compounds suffer from disadvantages including relying on multi-step conditions, the use of toxic organic solvents or catalysts containing transition metals, tedious work-up procedure, troublesome waste discarding, high reaction time, and low yields [12-21]. The present methodology, not only, has not above limitation but most benefit to allocate to its that makes this method an instrumental alternative to the previous methodologies for these one-pot three-component reactions. One of the most advantages of these ionic liquid is its ability to be recyclable as a reaction medium. The reusability of the $Li(OHCH_2CH_2NH_2)$ (CF_3OAC) is of great importance from synthetic and economical points of view. The ionic liquid is recovered from the aqueous extracts of the reaction mixtures by evaporation of water under reduced pressure. As shown in Figure 2, the recovered catalyst can be reused at least five times in subsequent reactions without significant loss in the product yield.

Table 6. Influence of different catalysts in the synthesis of 3,4-dihydropyrano[*c*]chromenes.



1a **2** **3** **4a**

Entry	Conditions	Time (min)	Yield (%)^b	Ref.
1	TMGT	60	79	[12]
2	γ-Fe_2O_3@HAp-Si-$(CH_2)_3$-AMP	10	78	[13]
3	TBAB	40	88	[14]
4	SDS	120	88	[15]
5	DBU	7	92	[16]
6	$H_6[P_2W_{18}O_{62}].18H_2O$	30	89	[17]
7	DAHP	240	95	[18]
8	Nano aluminum hydroxide	15	92	[19]
9	CuO nanoparticles	6	93	[20]
10	$RuBr_2(pph_3)_4$	3	80	[21]
11	$Li(OHCH_2CH_2NH_2)(CF_3OAC)$	5	94	This work

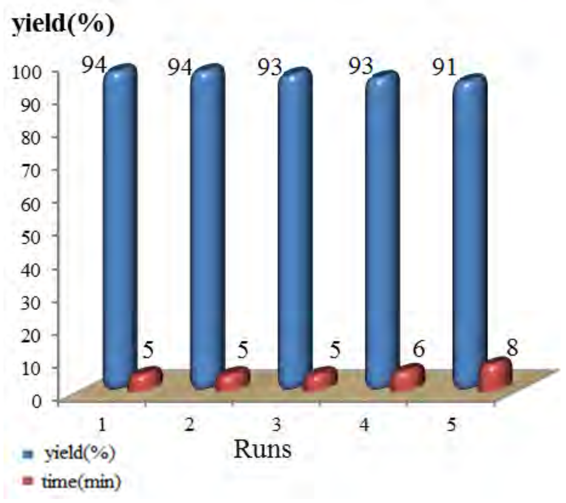


Fig. 2. Reusability of the catalyst.

We propose the following mechanism to account for the synthesis of 2-amino-*4H*-chromene derivatives. In the first step, malonitrile reacts quite quantitatively with aromatic aldehyde in a Knoevenagel transformation to afford the a-cyanocinnamonitrile derivative **7**. Presumably, the efficient catalysis effect of Li(OHCH$_2$CH$_2$NH$_2$) (CF$_3$OAC) is related to its acid-base functions as well as to providing tuned ionic medium. In the second step, the active methylene of 1,3 diketone **1** reacts with the electrophilic C=C double bond in **7** giving the intermediate **8**. Then, it is cyclized by nucleophilic attack of the carbonyl group on cyano group giving intermediate **9**. Finally, the expected products **4, 5** and **6** are afforded by tautomerization (Scheme 2).

4. Conclusions

In summary, a one-pot three-component method for the synthesis of 2-amino-4*H*-chromene derivatives using the reaction of different enols, aldehydes, and malononitrile in the ionic liquid Li(OHCH$_2$CH$_2$NH$_2$)(CF$_3$OAC) was introduced. The mild reaction conditions, simplicity of the procedure, and reusability of the catalyst offer improvements over many existing methods.

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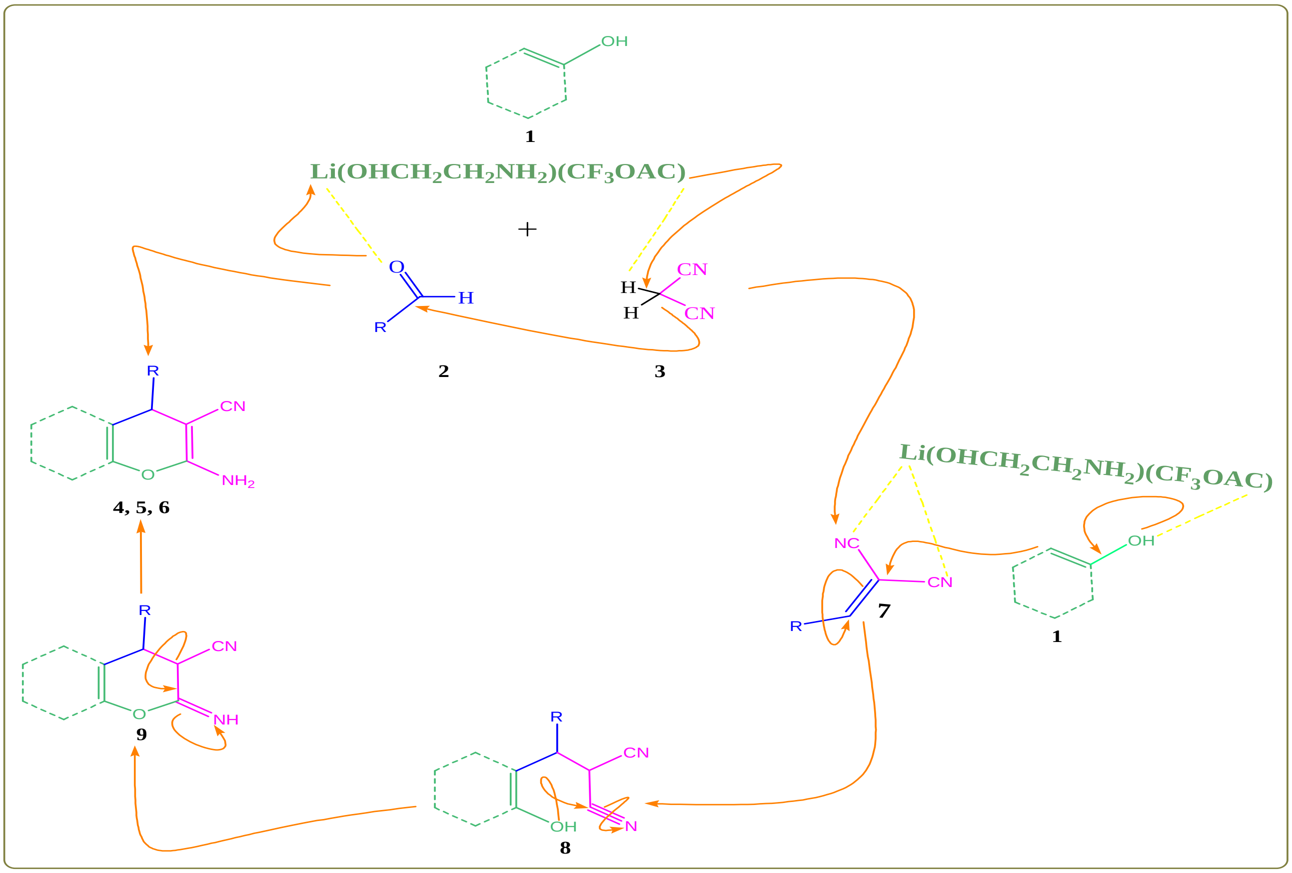

Scheme 2. A plausible mechanism for the synthesis of products **4, 5** and **6**.

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